

Polythiophene thin films deposited in various RF plasma polymerization configurations

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Abstract: Direct discharge and postdischarge RF plasma systems have been configured for plasma polymerization of thiophene. The monomer is fragmented in plasma and polymerize in gas phase (OES and MS data); chemical groups similar to the ones in thiophene, but also related to the formation of different oligomers are observed (FTIR, XPS data) on substrate. Electrical measurements show a significant improvement of conductivity upon iodine doping.

Keywords: plasma polymerization, RF direct discharge, remote RF plasma, polythiophene

1. Introduction

The discovery of conducting polymers opened up a wide range of possibilities for developing devices combining unique optical, electrical, and mechanical properties [1]. Already field effect transistors, rechargeable batteries, and photovoltaics, antistatic coatings, light-emitting diodes, sensors based on polymeric layers have created a growing market based on organic electronics [2-3]. Most of them are based on derivatives of polythiophene (e.g Poly(3,4-ethylenedioxythiophene) – PEDOT), polyaniline (PANI) or polypyrrole [4]. A key property of a conductive polymer is the presence of conjugated double bonds along the backbone of the polymer. In addition charge carriers in the form of extra electrons or “holes” have to be injected into the material for improving the conductivity characteristics.

Plasma polymerization proved to be an alternative technique to the classical polymerization for obtaining polymer-like thin films with good adherence and conformality to the substrate [5]. The main drawback in this case is related to the presence of the energetic species in the plasma which dissociate the precursors and so the obtained materials contains only in a small extent the original bonding environment. Therefore the challenge in using plasma polymerization for obtaining conductive polymers is to find proper configurations and deposition conditions to preserve the conjugated double bonds.

This contribution presents results regarding the deposition of polythiophene-like thin films in RF plasma configurations with limited reactivity, by working at low power levels, using pulsed plasma, or in remote plasma conditions. The influence of post-deposition iodine doping was also investigated.

2. Experimental

The configurations used for the plasma polymer depositions are schematically presented in Figure 1.

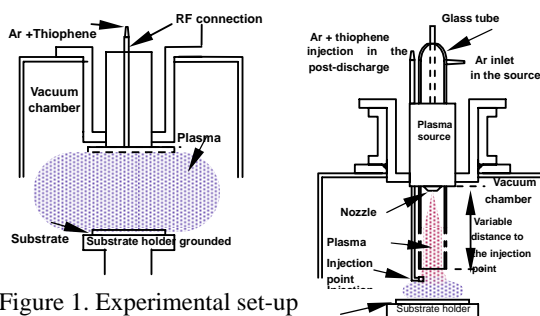


Figure 1. Experimental set-up

a) direct discharge configuration; b) postdischarge configuration

On the left, a classical configuration with parallel-plate RF electrodes (so-called – direct discharge configuration) was used [6]. The upper electrode, RF active (applied powers in the range 5-35 W) was constructed as a shower allowing the homogeneous introduction of the argon/thiophene vapors in the reactor, while the bottom one, grounded, was accommodating the substrate. In order to preserve the chemical structure of thiophene, pulsed plasma with duty cycle in the range 15 - 85% has been used.

Also in figure 1 is presented the remote plasma configuration used. In this case, the discharge was generated in argon flow (10 -100 sccm) in a small volume chamber and expanded in the main processing chamber through a small nozzle performed in the bottom electrode [7]. Glass tubes of variable lengths were mounted at the level of plasma generation zone exit to diminish the loss of active species by transport and quenching at the metallic wall of the chamber. The thiophene vapors were carried in the reactor by a small flow of Ar (5 sccm) and injected downstream, at variable distances from the plasma generation zone, while the distance between the precursor injection point and the substrate was maintained constant in all the experiments.

For precise control of the monomer flow, a CEM

(control, evaporation and mixing) system has been used; it combines a small Ar carrier flow (5-20 sccm) with the vaporized thiophene flow (0.5 – 2 g/h, vaporization temperature 40 °C) and provide a constant combined flow.

The as- deposited polythiophene-like thin films obtained in both configurations have been exposed to iodine vapors for 1 – 80 min. The iodine atoms are incorporated into film in order to improve the conductivity of the polymeric materials obtained in plasma.

Plasma species have been investigated by Optical Emission Spectroscopy (OES) and Mass Spectrometry (MS), while the material properties have been studied by Atomic Force Microscopy (AFM), Fourier Transform Infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), spectroscopic ellipsometry, and conductivity measurements techniques.

3. Results and discussion

3.1. Plasma characterization

Optical emission spectroscopy of the discharge generated in argon/thiophene mixture in parallel-plate configuration show the quenching of Ar lines and the presence of the CS radical $A^1\Pi-X^1\Sigma^+$ with the band head (0,0) at 257.6 nm (see Figure 2), while no emission related to CH, C₂, S₂ or SH could be determined. In the remote plasma configuration, the CS emission is much weaker due to the lower density of excited particles. This proves that the density of active species is lower and it is expected that their mixing with the monomer will produce

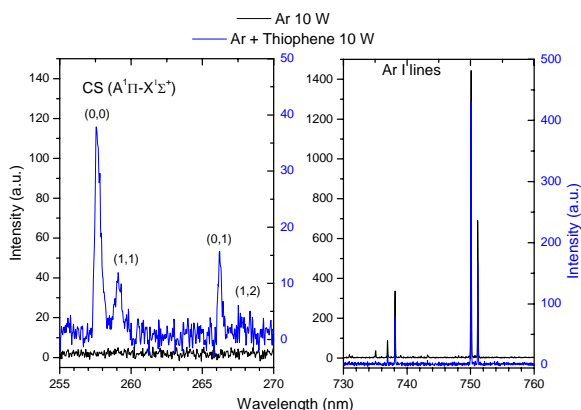


Figure 2. Spectra of direct discharge at the substrate level with (blue curve) and without thiophene (black curve)

less fragmentation (so a better conservation of initial monomer bonds).

Figure 3 presents the mass spectra of Ar/thiophene mixture with and without plasma in the case of direct discharge. Besides the main peaks at 84 m/e and 40 m/e, which are clearly assigned to thiophene monomer and respectively to argon, the other peaks in the plasma OFF situation (situated at 39, 45, 58) are related to the

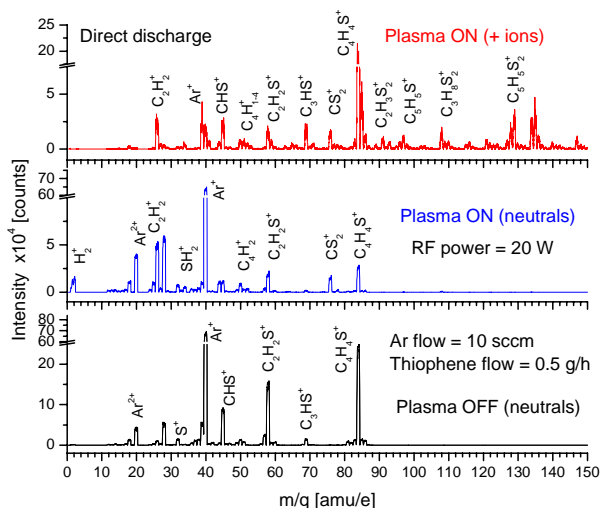


Figure 3. MS spectra of Ar/thiophene mixture in direct discharge precursor fragmentation which takes place inside the mass spectrometer. Formation of new neutral radicals is observed when the plasma is ignited, all having masses below that of thiophene (H₂, SH₂, CS₂). In the positive ions mass spectra a lot of peaks are appearing also at m/e above 84, pointing out towards the existence of gas phase polymerization processes which lead to formation of large mass oligomers. Comparatively, as can be seen from Figure 4 in the MS of postdischarge, only neutral particles

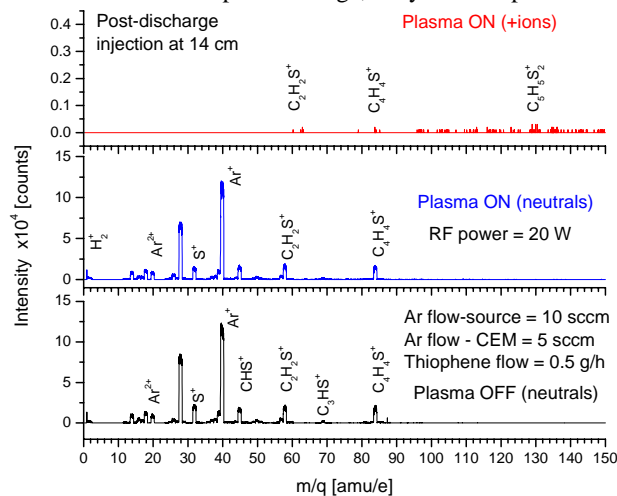


Figure 4. MS spectra of Ar/thiophene mixture in postdischarge

are present, therefore the dissociation of thiophene is taking place mostly through the interaction with metastable species coming from discharge, which are still present at injection level. A small signal coming from the positive ions in postdischarge plasma can be measured only when working at much higher Ar flow through the plasma source (100 sccm) and higher RF powers (above 50 W).

3.2. Material characterization

Spectroscopic ellipsometry data have been interpreted by using a Cauchy model [8] which provided a good fit in the spectral region where the film is transparent (500 – 1700 nm), allowing the determination of films thicknesses and their dispersion of refractive index. The deposition rate in both configurations is increasing with the applied RF power, but remains almost constant under pulsed plasma, proving that the monomer grafting during the plasma OFF time is very limited. The deposition rate for thin films deposited in similar conditions (RF = 20 W, Ar flow 10 sccm, thiophene flow = 0.5 g/h) but in different discharge configurations is around 29 nm/min in direct discharge, while in postdischarge is decreasing to 15.4 nm/min when the injection point is situated at 8 cm from the discharge zone and as low as 0.4 nm/min when the distance to injection is increased to 14 cm. One must mention that the thickness values obtained by ellipsometry are very similar (within an error of maximum 5%) to the ones provided by AFM technique, where a sharp edge was insured between plasma polymerized film and the bare Si substrate.

The surface topography, as resulted from AFM measurements, is significantly dependent on the used configuration and the plasma condition, namely continuous, pulsed, direct or remote discharge. The samples deposited at large thiophene flows (2 – 4 g/h) present in case of continuous plasma a large number of particulates on the surface, the average roughness being around 30 nm (not shown). Instead, by using pulsed plasma (see Figure 5 – left), the surface aspect is improved and the roughness is decreasing. Lower RMS values can be obtained also in continuous plasma if lower thiophene flows, as proved by Figure 5 – right where 0.5 g/h were used. The samples

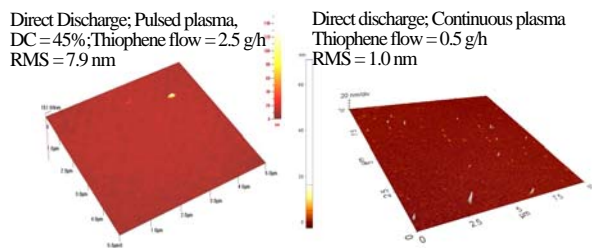


Figure 5. AFM pictures of samples deposited pulsed and continuous plasma in direct discharge; RF power = 20 W

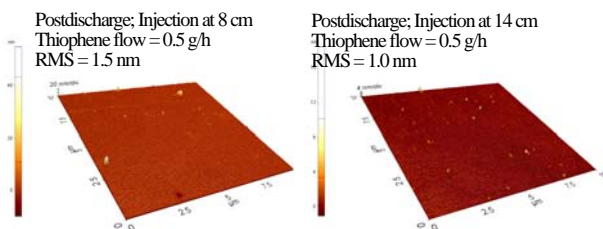


Figure 6. AFM pictures of samples deposited pulsed and continuous plasma in postdischarge; RF power = 20 W

deposited in postdischarge configuration are very smooth, as can be noticed from Figure 6.

A typical FTIR spectrum of polythiophene-like thin films obtained in direct discharge is presented in Figure 7. It shows the presence of specific thiophene bonds in the region 600 – 700 cm^{-1} associated to C-S bonds and those in the region 1550 – 1590 cm^{-1} due to the ring vibration [9,10]. Also, the peaks from 3060 and 3100 cm^{-1} are corresponding to the α -H and β -H bonds in thiophene ring [11]. On the other hand, the peak at 1685 cm^{-1} corresponding to C=S vibration, the large absorption band at 2700 – 3000 cm^{-1} coming from the CH₂ and CH₃ stretching bonds and the well defined peak at 3288 cm^{-1} attrib-

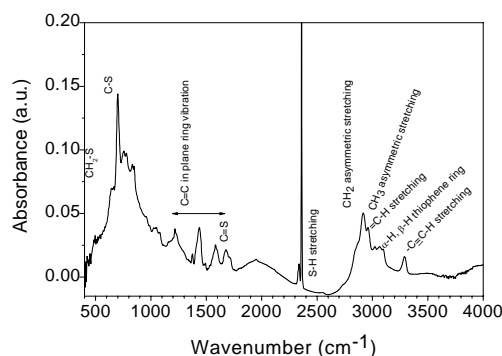


Figure 7. Typical FTIR spectrum of plasma-polythiophene film deposited in direct discharge configuration

uted to $\text{-C}\equiv\text{C-H}$ prove the existence of different oligomers in the deposited film. It shows as well that the polymerization of fragments formed in the plasma in the gas phase, as seen from the mass spectrometry data, are contributing to some extent to the film growth. As result, the C, S and H atoms are bonded in different configurations in respect to those in thiophene monomer.

The XPS measurements for the regions corresponding to the bonding energy of C1s and S2p are presented in Figure 8. In the C 1s region, the obtained signal can be deconvoluted in three peaks corresponding to thiophene-like bond at 285 eV, CS₂ at 286.43 eV and C-O bond at 287.66 eV related to postdeposition oxidation of sample. In the S2p region, the presence of CS₂ bond was also determined. Additional peaks are appearing for the iodine doped samples (not shown) both in the C1s region (at 288.09 eV) and in the S2p region (168.82 eV), correlated with a decrease of the oxygen-related peak. These confirm the iodine presence on the sample surface and the limited degradation upon air exposure for the grafted surfaces.

The resistivity has been determined by van der Pauw method for samples deposited in direct discharge (DD) and postdischarge (PD) configurations, for fresh prepared samples and iodine doped ones. The results are presented in Table 1, where the thiophene flow was constant for all samples at 0.5 g/h, and the applied RF power was set to

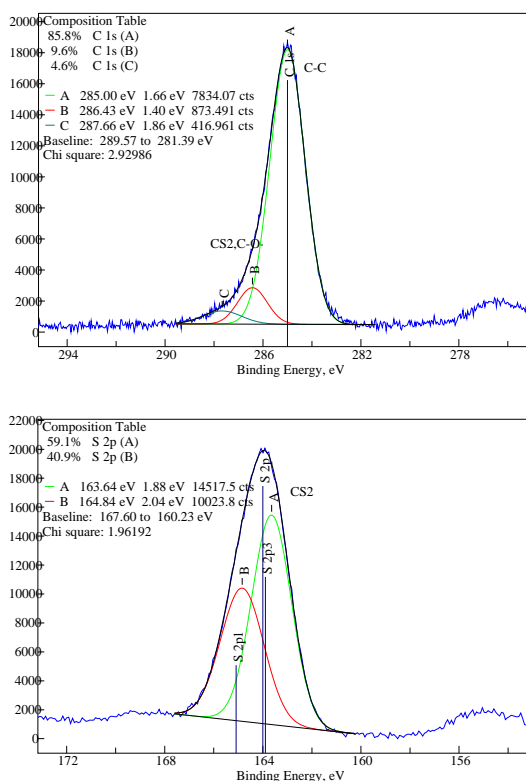


Figure 8. XPS spectra in the region of C1s and S2p bonding energy 20 W. The as-deposited samples and the iodated samples at low exposure time (~5 min) are presenting quite large resistivity (in the order of 10^9 - 10^8 Ω cm) in both discharge configurations; instead, the iodine doped samples at long exposure time (30 min) leads to improved electrical properties, up to 2.02×10^4 Ω cm for sample deposited in post-discharge configuration at intermediate injection distance.

Table 1. Resistivity values for samples deposited in direct discharge (DD) and postdischarge (PD) at constant thiophene flow (0.5 g/h) and constant RF power (20 W)

Discharge type	Ar flow	Ar flow	Injection distance	Iodine exposure time min	Resistivity Ω cm
	**	_**_			
	sccm	sccm	cm		
DD	10	N/A	N/A	NO	1.90×10^9
DD	10	N/A	N/A	30	7.39×10^4
PD	5	10	2	NO	1.33×10^8
PD	5	10	2	5	1.07×10^8
PD	5	10	2	30	1.37×10^5
PD	5	30	8	NO	3.49×10^9
PD	5	30	8	30	2.02×10^4

* through the CEM injection system

**through the postdischarge plasma source

Conclusions

Polythiophene thin films have been obtained by plasma polymerization in direct discharge and postdischarge RF plasma configurations. Plasma investigations prove the dissociation and excitation of precursor in both configurations and the formation of new oligomers with various masses in gas phase. Under specific conditions, very smooth films can be obtained at convenient deposition rates (30 nm/min). The chemical composition, as determined by FTIR and XPS measurements, point out that the grown material contain in a limited amount the initial bonding environment as in thiophene monomer, but also new chemical bonds created during plasma polymerization process. The as-deposited samples are quite resistive, but the iodine-doped material presents conductivity values with up to 5 orders of magnitude improved.

Acknowledgements

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